CASE H 4132 PCT/US

Cosmetic or Pharmaceutical Utilization of Nanoscalic Metal Soaps

This invention relates generally to nanoparticles and more particularly to the use of nanoscale metal soaps in cosmetics.

Prior Art

In the cosmetics field, metal soaps such as, for example, magnesium or aluminium stearates are mainly used as stabilizers for the production of o/w and preferably w/o emulsions. They are also used as opacifiers and - above all in combination with fatty alcohols - as consistency factors. However, a disadvantage of known metal soaps is that they are not entirely satisfactory either in their stabilizing function or in their consistency factor function. Accordingly, the problem addressed by the present invention was to provide metal soaps in a new supply form with which the problems mentioned above could be satisfactorily solved.

Description of the Invention

The present invention relates to the use of nanoscale metal soaps in the 10 to 300 nm range for the production of cosmetic and/or pharmaceutical preparations.

It has surprisingly been found that both the stability of lotions and creams and their consistency is significantly improved by the addition of metal soaps providing the metal soaps are present in the form of nanoparticles, i.e. particles with a mean diameter of 10 to 300 and preferably 50 to 150 nm. At the same time, preparations with a more intensive white opacity are obtained.

Metal soaps

The metal soaps are known salts of fatty acids which preferably

correspond to formula (I):

$(R^1COO)_nX$ (I)

in which R^1CO is a linear or branched, saturated or unsaturated, optionally hydroxysubstituted acyl group containing 6 to 22 carbon atoms and X is an alkali metal or alkaline earth metal, aluminium or zinc and n is a number corresponding to the valency of X. Typical examples are the sodium, potassium, calcium, magnesium, aluminium and zinc salts of caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, ricinoleic acid, 12-hydroxystearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and technical mixtures thereof. The use of magnesium stearate and magnesium-12-hydroxystearate, aluminium stearate and aluminium-12-hydroxystearate and zinc stearate and zinc-12-hydroxystearate is particularly preferred.

Production of nanoparticles

One process for the production of nanoparticles by **rapid expansion of supercritical solutions (RESS)** is known from the article by S. Chihlar, M. Türk and K. Schaber in **Proceedings World Congress on Particle Technology 3, Brighton, 1998**. A preferred embodiment of the present invention is characterized by the use of metal soaps obtained by

(a) dissolving the starting materials in a suitable solvent under supercritical or near-critical conditions,

(b) expanding the fluid mixture through a nozzle into a vacuum, a gas or a liquid and

(c) simultaneously evaporating the solvent.

To prevent the nanoparticles from agglomerating, it is advisable to dissolve

the starting materials in the presence of suitable protective colloids or emulsifiers and/or to expand the critical solutions into aqueous and/or alcoholic solutions of the protective colloids or emulsifiers or into cosmetic oils which may in turn contain redissolved emulsifiers and/or protective colloids. Suitable protective colloids are, for example, gelatine, casein, chitosan, gum arabic, lysalbinic acid, starch and polymers, such as polyvinyl alcohols, polyvinyl pyrrolidones, polyalkylene glycols and polyacrylates. Accordingly, the nanoscale organic metal soaps preferably used are those which are surrounded by a protective colloid and/or an emulsifier. The protective colloids or emulsifiers are normally used in quantities of 0.1 to 20% by weight and preferably in quantities of 5 to 15% by weight, based on the metal soaps.

Another suitable process for the production of nanoscale particles is the **evaporation technique**. Here, the starting materials are first dissolved in a suitable organic solvent (for example alkanes, vegetable oils, ethers, esters, ketones, acetals and the like). The resulting solutions are then introduced into water or another non-solvent, optionally in the presence of a surface-active compound dissolved therein, in such a way that the nanoparticles are precipitated by the homogenization of the two immiscible solvents, the organic solvent preferably evaporating. O/w emulsions or o/w microemulsions may be used instead of an aqueous solution. The emulsifiers and protective colloids mentioned at the beginning may be used as the surface-active compounds. Another method for the production of nanoparticles is the so-called **GAS process** (gas anti-solvent recrystallization). This process uses a highly compressed gas or supercritical fluid (for example carbon dioxide) as non-solvent for the crystallization of dissolved substances. The compressed gas phase is introduced into the primary solution of the starting materials and absorbed therein so that there is an increase in the liquid volume and a reduction in solubility and fine particles are precipitated. The **PCA process**

(precipitation with a compressed fluid anti-solvent) is equally suitable. In this process, the primary solution of the starting materials is introduced into a supercritical fluid which results in the formation of very fine droplets in which diffusion processes take place so that very fine particles are precipitated. In the **PGSS process** (particles from gas saturated solutions), the starting materials are melted by the introduction of gas under pressure (for example carbon dioxide or propane). Temperature and pressure reach near- or super-critical conditions. The gas phase dissolves in the solid and lowers the melting temperature, the viscosity and the surface tension. On expansion through a nozzle, very fine particles are formed as a result of cooling effects.

Commercial Applications

Compared with known metal soaps, the particular fineness of the particles provides for greater stability and consistency of the emulsions. Accordingly, the present invention also relates to the use of the nanoscale metal soaps for the production of cosmetic and/or pharmaceutical preparations, more particularly hair and skin treatment preparations. The metal soaps are normally used in a quantity of 0.1 to 5% by weight, preferably in a quantity of 0.5 to 3% by weight and more preferably in a quantity of 1 to 2% by weight, based on the preparations.

Cosmetic and/or pharmaceutical preparations

The nanoscale metal soaps to be used in accordance with the invention may be used for the production of cosmetic and/or pharmaceutical preparations, for example hair shampoos, hair lotions, foam baths, shower baths, creams, gels, lotions, alcoholic and aqueous/ alcoholic solutions, emulsions, wax/fat compounds, stick preparations, powders or ointments. These preparations may also contain mild surfactants, oil components, emulsifiers, superfatting agents, pearlizing

waxes, consistency factors, thickeners, polymers, silicone compounds, fats, waxes, biogenic agents, deodorizers, antiperspirants, antidandruff agents, film formers, swelling agents, UV protection factors, antioxidants, hydrotropes, preservatives, insect repellents, self-tanning agents, solubilizers, perfume oils, dyes and the like as further auxiliaries and additives.

Typical examples of suitable mild, i.e. particularly dermatologically compatible, **surfactants** are fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or dialkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates, α-olefin sulfonates, ether carboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamidobetaines and/or protein fatty acid condensates, preferably based on wheat proteins.

Suitable **oil components** are, for example, Guerbet alcohols based on fatty alcohols containing 6 to 18 and preferably 8 to 10 carbon atoms, esters of linear C_{6-22} fatty acids with linear C_{6-22} fatty alcohols, esters of branched C_{6-13} carboxylic acids with linear C_{6-22} fatty alcohols such as, for example, myristyl myristate, myristyl palmitate, myristyl stearate, myristyl isostearate, myristyl oleate, myristyl behenate, myristyl erucate, cetyl myristate, cetyl palmitate, cetyl stearate, cetyl isostearate, cetyl oleate, cetyl behenate, cetyl erucate, stearyl myristate, stearyl palmitate, stearyl stearate, stearyl isostearate, stearyl oleate, stearyl behenate, stearyl erucate, isostearyl myristate, isostearyl palmitate, isostearyl stearate, isostearyl isostearate, isostearyl oleate, isostearyl behenate, isostearyl oleate, oleyl myristate, oleyl palmitate, oleyl stearate, oleyl isostearate, oleyl oleate, oleyl behenate, oleyl erucate, behenyl myristate, behenyl palmitate, behenyl stearate, behenyl isostearate, behenyl oleate, behenyl behenate, behenyl erucate, erucyl myristate, erucyl palmitate, erucyl stearate, erucyl isostearate, erucyl oleate, erucyl behenate and erucyl erucate. Also suitable are esters of linear C_{6-22} fatty acids with branched

alcohols, more particularly 2-ethyl hexanol, esters of hydroxycarboxylic acids with linear or branched C_{6-22} fatty alcohols, more especially Dioctyl Malate, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, triglycerides based on C_{6-10} fatty acids, liquid mono-/di-/triglyceride mixtures based on C_{6-18} fatty acids, esters of C_{6-22} fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, more particularly benzoic acid, esters of C_{2-12} dicarboxylic acids with linear or branched alcohols containing 1 to 22 carbon atoms or polyols containing 2 to 10 carbon atoms and 2 to 6 hydroxyl groups, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear and branched C_{6-22} fatty alcohol carbonates, Guerbet carbonates, esters of benzoic acid with linear and/or branched C_{6-22} alcohols (for example Finsolv® TN), linear or branched, symmetrical or nonsymmetrical dialkyl ethers containing 6 to 22 carbon atoms per alkyl group, ring opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons, for example squalane, squalene or dialkyl cyclohexanes.

Suitable **emulsifiers** are, for example, nonionic surfactants from at least one of the following groups:

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear C_{8-22} fatty alcohols, C_{12-22} fatty acids and alkyl phenols containing 8 to 15 carbon atoms in the alkyl group and alkylamines containing 8 to 22 carbon atoms in the alkyl group;
- alkyl and/or alkenyl oligoglycosides containing 8 to 22 carbon atoms in the alk(en)yl group and ethoxylated analogs thereof;
- adducts of 1 to 15 moles of ethylene oxide with castor oil and/or hydrogenated castor oil;
- adducts of 15 to 60 moles of ethylene oxide with castor oil and/or

hydrogenated castor oil;

- partial esters of glycerol and/or sorbitan with unsaturated, linear or saturated, branched fatty acids containing 12 to 22 carbon atoms and/or hydroxycarboxylic acids containing 3 to 18 carbon atoms and adducts thereof with 1 to 30 moles of ethylene oxide;
- partial esters of polyglycerol (average degree of self-condensation 2 to 8), polyethylene glycol (molecular weight 400 to 5000), trimethylolpropane, pentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose) with saturated and/or unsaturated, linear or branched fatty acids containing 12 to 22 carbon atoms and/or hydroxycarboxylic acids containing 3 to 18 carbon atoms and adducts thereof with 1 to 30 moles of ethylene oxide;
- mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol according to **DE-PS 11 65 574** and/or mixed esters of fatty acids containing 6 to 22 carbon atoms, methyl glucose and polyols, preferably glycerol or polyglycerol,
- mono-, di- and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and salts thereof,
- wool wax alcohols,
- polysiloxane/polyalkyl/polyether copolymers and corresponding derivatives,
- polyalkylene glycols and
- glycerol carbonate.

The **addition products of ethylene oxide and/or propylene oxide** with fatty alcohols, fatty acids, alkylphenols or with castor oil are known commercially available products. They are homolog mixtures of which the average degree of alkoxylation corresponds to the ratio between the

quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. $C_{12/18}$ fatty acid monoesters and diesters of adducts of ethylene oxide with glycerol are known as refatting agents for cosmetic formulations from **DE-PS 20 24 051**.

Alkyl and/or alkenyl oligoglycosides, their production and their use are known from the prior art. They are produced in particular by reacting glucose or oligosaccharides with primary alcohols containing 8 to 18 carbon atoms. So far as the glucoside unit is concerned, both monoglycosides in which a cyclic sugar unit is attached to the fatty alcohol by a glycoside bond and oligomeric glycosides with a degree of oligomerization of preferably up to about 8 are suitable. The degree of oligomerization is a statistical mean value on which the homolog distribution typical of such technical products is based.

Typical examples of suitable **partial glycerides** are hydroxystearic acid monoglyceride, hydroxystearic acid diglyceride, isostearic acid monoglyceride, isostearic acid diglyceride, oleic acid monoglyceride, oleic acid diglyceride, ricinoleic acid monoglyceride, ricinoleic acid diglyceride, linoleic acid monoglyceride, linoleic acid diglyceride, linolenic acid monoglyceride, linolenic acid diglyceride, erucic acid monoglyceride, erucic acid diglyceride, tartaric acid monoglyceride, tartaric acid diglyceride, citric acid monoglyceride, citric acid diglyceride, malic acid monoglyceride, malic acid diglyceride and technical mixtures thereof which may still contain small quantities of triglyceride from the production process. Addition products of 1 to 30 and preferably 5 to 10 moles of ethylene oxide with the partial glycerides mentioned are also suitable.

Suitable **sorbitan esters** are sorbitan monoisostearate, sorbitan sesquiisostearate, sorbitan diisostearate, sorbitan triisostearate, sorbitan monooleate, sorbitan sesquioleate, sorbitan dioleate, sorbitan trioleate, sorbitan monoerucate, sorbitan sesquierucate, sorbitan dierucate, sorbitan trierucate, sorbitan monoricinoleate, sorbitan sesquiricinoleate, sorbitan

diricinoleate, sorbitan triricinoleate, sorbitan monohydroxystearate, sorbitan sesquihydroxystearate, sorbitan dihydroxystearate, sorbitan trihydroxystearate, sorbitan monotartrate, sorbitan sesquitartrate, sorbitan ditartrate, sorbitan tritartrate, sorbitan monocitrate, sorbitan sesquicitrate, sorbitan dicitrate, sorbitan tricitrate, sorbitan monomaleate, sorbitan sesquimaleate, sorbitan dimaleate, sorbitan trimaleate and technical mixtures thereof. Addition products of 1 to 30 and preferably 5 to 10 moles of ethylene oxide with the sorbitan esters mentioned are also suitable.

Typical examples of suitable **polyglycerol esters** are Polyglyceryl-2 Dipolyhydroxystearate (Dehymuls® PGPH), Polyglycerin-3-Diisostearate (Lameform® TGI), Polyglyceryl-4 Isostearate (Isolan® GI 34), Polyglyceryl-3 Oleate, Diisostearoyl Polyglyceryl-3 Diisostearate (Isolan® PDI), Polyglyceryl-3 Methylglucose Distearate (Tego Care® 450), Polyglyceryl-3 Beeswax (Cera Bellina®), Polyglyceryl-4 Caprate (Polyglycerol Caprate T2010/90), Polyglyceryl-3 Cetyl Ether (Chimexane® NL), Polyglyceryl-3 Distearate (Cremophor® GS 32) and Polyglyceryl Polyricinoleate (Admul® WOL 1403), Polyglyceryl Dimerate Isostearate and mixtures thereof.

Examples of other suitable **polyolesters** are the mono-, di- and triesters of trimethylol propane or pentaerythritol with lauric acid, cocofatty acid, tallow fatty acid, palmitic acid, stearic acid, oleic acid, behenic acid and the like optionally reacted with 1 to 30 moles of ethylene oxide.

Other suitable emulsifiers are **zwitterionic surfactants**. Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as the N-alkyl-N,N-dimethyl ammonium glycinates, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinates, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon

atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known under the CTFA name of *Cocamidopropyl Betaine* is particularly preferred. Ampholytic surfactants are also suitable emulsifiers. Ampholytic surfactants are surface-active compounds which, in addition to a $C_{8/18}$ alkyl or acyl group, contain at least one free amino group and at least one -COOH- or -SO_3H- group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethyl aminopropionate and $C_{12/18}$ acyl sarcosine.

Finally, other suitable emulsifiers are **cationic surfactants**, those of the esterquat type, preferably methyl-quaternized difatty acid triethanolamine ester salts, being particularly preferred.

Superfatting agents may be selected from such substances as, for example, lanolin and lecithin and also polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the fatty acid alkanolamides also serving as foam stabilizers

Suitable **pearlizing waxes** are, for example, alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanolamides, especially cocofatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polybasic, optionally hydroxysubstituted carboxylic acids with fatty alcohols containing 6 to 22 carbon atoms, especially long-chain esters of tartaric acid; fatty compounds, such as for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates which contain in all at least 24 carbon atoms, especially laurone

and distearylether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring opening products of olefin epoxides containing 12 to 22 carbon atoms with fatty alcohols containing 12 to 22 carbon atoms and/or polyols containing 2 to 15 carbon atoms and 2 to 10 hydroxyl groups and mixtures thereof.

The **consistency factors** mainly used are fatty alcohols or hydroxyfatty alcohols containing 12 to 22 and preferably 16 to 18 carbon atoms and also partial glycerides, fatty acids or hydroxyfatty acids. A combination of these substances with alkyl oligoglucosides and/or fatty acid N-methyl glucamides of the same chain length and/or polyglycerol poly-12-hydroxystearates is preferably used.

Suitable **thickeners** are, for example, Aerosil® types (hydrophilic silicas), polysaccharides, more especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, also relatively high molecular weight polyethylene glycol mono- esters and diesters of fatty acids, polyacrylates (for example Carbopols® [Goodrich] or Synthalens® [Sigma]), polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as, for example, ethoxylated fatty acid glycerides, esters of fatty acids with polyols, for example pentaerythritol or trimethylol propane, narrow-range fatty alcohol ethoxylates or alkyl oligoglucosides and electrolytes, such as sodium chloride and ammonium chloride.

Suitable **cationic polymers** are, for example, cationic cellulose derivatives such as, for example, the quaternized hydroxyethyl cellulose obtainable from Amerchol under the name of Polymer JR 400®, cationic starch, copolymers of diallyl ammonium salts and acrylamides, quaternized vinyl pyrrolidone/vinyl imidazole polymers such as, for example, Luviquat® (BASF), condensation products of polyglycols and amines, quaternized collagen polypeptides such as, for example, Lauryldimonium Hydroxypropyl Hydrolyzed Collagen (Lamequat® L, Grünau), quaternized wheat

polypeptides, polyethyleneimine, cationic silicone polymers such as, for example, amodimethicone, copolymers of adipic acid and dimethylaminohydroxypropyl diethylenetriamine (Cartaretine®, Sandoz), copolymers of acrylic acid with dimethyl diallyl ammonium chloride (Merquat® 550, Chemviron), polyaminopolyamides as described, for example, in **FR 2 252 840 A** and crosslinked water-soluble polymers thereof, cationic chitin derivatives such as, for example, quaternized chitosan, optionally in microcrystalline distribution, condensation products of dihaloalkyls, for example dibromobutane, with bis-dialkylamines, for example bis-dimethylamino-1,3-propane, cationic guar gum such as, for example, Jaguar®CBS, Jaguar®C-17, Jaguar®C-16 of Celanese, quaternized ammonium salt polymers such as, for example, Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 of Miranol.

Suitable **anionic, zwitterionic, amphoteric and nonionic polymers** are, for example, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinylether/maleic anhydride copolymers and esters thereof, uncrosslinked and polyol-crosslinked polyacrylic acids, acrylamidopropyl trimethylammonium chloride/acrylate copolymers, octylacrylamide/methyl methacrylate/tert.-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, vinyl pyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and optionally derivatized cellulose ethers and silicones.

Suitable **silicone compounds** are, for example, dimethyl polysiloxanes, methylphenyl polysiloxanes, cyclic silicones and amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds which may be both liquid and resin-like at room temperature. Other suitable silicone compounds are simethicones which are mixtures of dimethicones with an average chain length of 200 to 300

dimethylsiloxane units and hydrogenated silicates. A detailed overview of suitable volatile silicones can be found in Todd et al. in **Cosm. Toil. 91, 27 (1976)**.

Typical examples of **fats** are glycerides while suitable **waxes** are inter alia natural waxes such as, for example, candelilla wax, carnauba wax, Japan wax, espartograss wax, cork wax, guaruma wax, rice oil wax, sugar cane wax, ouricury wax, montan wax, beeswax, shellac wax, spermaceti, lanolin (wool wax), uropygial fat, ceresine, ozocerite (earth wax), petrolatum, paraffin waxes, microwaxes; chemically modified waxes (hard waxes) such as, for example, montan ester waxes, sasol waxes, hydrogenated jojoba waxes and synthetic waxes such as, for example, polyalkylene waxes and polyethylene glycol waxes.

In the context of the invention, **biogenic agents** are, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts and vitamin complexes.

Cosmetic **deodorants** counteract, mask or eliminate body odors. Body odors are formed through the action of skin bacteria on apocrine perspiration which results in the formation of unpleasant-smelling degradation products. Accordingly, deodorants contain active principles which act as germ inhibitors, enzyme inhibitors, odor absorbers or odor maskers.

Basically, suitable **germ inhibitors** are any substances which act against gram-positive bacteria such as, for example, 4-hydroxybenzoic acid and salts and esters thereof, N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl)-urea, 2,4,4'-trichloro-2'-hydroxydiphenylether (triclosan), 4-chloro-3,5-dimethylphenol, 2,2'-methylene-bis-(6-bromo-4-chlorophenol), 3-methyl-4-(1-methylethyl)-phenol, 2-benzyl-4-chlorophenol, 3-(4-chloro-phenoxy)-propane-1,2-diol, 3-iodo-2-propinyl butyl carbamate, chlor-

hexidine, 3,4,4'-trichlorocarbanilide (TTC), antibacterial perfumes, thymol, thyme oil, eugenol, nettle oil, menthol, mint oil, farnesol, phenoxyethanol, glycerol monolaurate (GML), diglycerol monocaprate (DMC), salicylic acid-N-alkylamides such as, for example, salicylic acid-n-octyl amide or salicylic acid-n-decyl amide.

Suitable **enzyme inhibitors** are, for example, esterase inhibitors. Esterase inhibitors are preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and, in particular, triethyl citrate (Hydagen® CAT, Henkel KGaA, Düsseldorf, FRG). Esterase inhibitors inhibit enzyme activity and thus reduce odor formation. Other esterase inhibitors are sterol sulfates or phosphates such as, for example, lanosterol, cholesterol, campesterol, stigmasterol and sitosterol sulfate or phosphate, dicarboxylic acids and esters thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester, hydroxycarboxylic acids and esters thereof, for example citric acid, malic acid, tartaric acid or tartaric acid diethyl ester, and zinc glycinate.

Suitable **odor absorbers** are substances which are capable of absorbing and largely retaining the odor-forming compounds. They reduce the partial pressure of the individual components and thus also reduce the rate at which they spread. An important requirement in this regard is that perfumes must remain unimpaired. Odor absorbers are not active against bacteria. They contain, for example, a complex zinc salt of ricinoleic acid or special perfumes of largely neutral odor known to the expert as "fixateurs" such as, for example, extracts of labdanum or styrax or certain abietic acid derivatives as their principal component. Odor maskers are perfumes or perfume oils which, besides their odor-masking function, impart their particular perfume note to the deodorants. Suitable perfume oils are, for example, mixtures of natural and synthetic fragrances. Natural

fragrances include the extracts of blossoms, stems and leaves, fruits, fruit peel, roots, woods, herbs and grasses, needles and branches, resins and balsams. Animal raw materials, for example civet and beaver, may also be used. Typical synthetic perfume compounds are products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Examples of perfume compounds of the ester type are benzyl acetate, p-tert.butyl cyclohexylacetate, linalyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. Ethers include, for example, benzyl ethyl ether while aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxy-citronellal, lilial and bourgeonal. Examples of suitable ketones are the ionones and methyl cedryl ketone. Suitable alcohols are anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenylethyl alcohol and terpineol. The hydrocarbons mainly include the terpenes and balsams. However, it is preferred to use mixtures of different perfume compounds which, together, produce an agreeable fragrance. Other suitable perfume oils are essential oils of relatively low volatility which are mostly used as aroma components. Examples are sage oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime-blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavendin oil. The following are preferably used either individually or in the form of mixtures: bergamot oil, dihydromyrcenol, lilial, lyral, citronellol, phenylethyl alcohol, α-hexylcinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, Boisambrene Forte, Ambroxan, indole, hedione, sandelice, citrus oil, mandarin oil, orange oil, allylamyl glycolate, cyclovertal, lavendin oil, clary oil, β-damascone, geranium oil bourbon, cyclohexyl salicylate, Vertofix Coeur, Iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat.

Antiperspirants reduce perspiration and thus counteract underarm wetness and body odor by influencing the activity of the eccrine sweat glands. Aqueous or water-free antiperspirant formulations typically contain the following ingredients:

- astringent active principles,
- oil components,
- nonionic emulsifiers,
- co-emulsifiers,
- consistency factors,
- auxiliaries in the form of, for example, thickeners or complexing agents and/or
- nonaqueous solvents such as, for example, ethanol, propylene glycol and/or glycerol.

Suitable astringent active principles of antiperspirants are, above all, salts of aluminium, zirconium or zinc. Suitable antihydrotic agents of this type are, for example, aluminium chloride, aluminium chlorohydrate, aluminium dichlorohydrate, aluminium sesquichlorohydrate and complex compounds thereof, for example with 1,2-propylene glycol, aluminium hydroxyallantoinate, aluminium chloride tartrate, aluminium zirconium trichlorohydrate, aluminium zirconium tetrachlorohydrate, aluminium zirconium pentachlorohydrate and complex compounds thereof, for example with amino acids, such as glycine. Oil-soluble and water-soluble auxiliaries typically encountered in antiperspirants may also be present in relatively small amounts. Oil-soluble auxiliaries such as these include, for example,

- inflammation-inhibiting, skin-protecting or pleasant-smelling essential oils,

- synthetic skin-protecting agents and/or
- oil-soluble perfume oils.

Typical water-soluble additives are, for example, preservatives, water-soluble perfumes, pH regulators, for example buffer mixtures, water-soluble thickeners, for example water-soluble natural or synthetic polymers such as, for example, xanthan gum, hydroxyethyl cellulose, polyvinyl pyrrolidone or high molecular weight polyethylene oxides.

Suitable **antidandruff agents** are climbazol, octopirox and zinc pyrithione.

Standard **film formers** are, for example, chitosan, microcrystalline chitosan, quaternized chitosan, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, polymers of the acrylic acid series, quaternary cellulose derivatives, collagen, hyaluronic acid and salts thereof and similar compounds.

Suitable **swelling agents** for aqueous phases are montmorillonites, clay minerals, Pemulen and alkyl-modified Carbopol types (Goodrich). Other suitable polymers and swelling agents can be found in R. Lochhead's review in **Cosm. Toil. 108, 95 (1993)**.

Examples of **UV protection factors** include organic substances (light filters) which are liquid or crystalline at room temperature and which are capable of absorbing ultraviolet radiation and of releasing the energy absorbed in the form of longer-wave radiation, for example heat. UV-B filters can be oil-soluble or water-soluble. The following are examples of oil-soluble substances:

- 3-benzylidene camphor or 3-benzylidene norcamphor and derivatives thereof, for example 3-(4-methylbenzylidene)-camphor, as described in **EP 0693471 B1**;
- 4-aminobenzoic acid derivatives, preferably 4-(dimethylamino)-benzoic

acid-2-ethylhexyl ester, 4-(dimethylamino)-benzoic acid-2-octyl ester and 4-(dimethylamino)-benzoic acid amyl ester;

- esters of cinnamic acid, preferably 4-methoxycinnamic acid-2-ethylhexyl ester, 4-methoxycinnamic acid propyl ester, 4-methoxycinnamic acid isoamyl ester, 2-cyano-3,3-phenylcinnamic acid-2-ethylhexyl ester (Octocrylene);
- esters of salicylic acid, preferably salicylic acid-2-ethylhexyl ester, salicylic acid-4-isopropylbenzyl ester, salicylic acid homomenthyl ester;
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone;
- esters of benzalmalonic acid, preferably 4-methoxybenzalmalonic acid di-2-ethylhexyl ester;
- triazine derivatives such as, for example, 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine and Octyl Triazone, as described in **EP 0 818 450 A1**, or Dioctyl Butamido Triazine (Uvasorb® HEB);
- propane-1,3-diones such as, for example, 1-(4-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione;
- ketotricyclo(5.2.1)decane derivatives, as described in **EP 0 694 521 B1**.

Suitable water-soluble substances are

- 2-phenylbenzimidazole-5-sulfonic acid and alkali metal, alkaline earth metal, ammonium, alkylammonium, alkanolammonium and glucammonium salts thereof;
- sulfonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and salts thereof;
- sulfonic acid derivatives of 3-benzylidene camphor such as, for example, 4-(2-oxo-3-bornylidenemethyl)-benzene sulfonic acid and 2-methyl-5-(2-oxo-3-bornylidene)-sulfonic acid and salts thereof.

Typical UV-A filters are, in particular, derivatives of benzoyl methane such as, for example 1-(4'-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione, 4-tert-butyl-4 -methoxydibenzoylmethane (Parsol 1789), 1-phenyl-3-(4'-isopropylphenyl)-propane-1,3-dione and the eneamine compounds described in **DE 19712033 A1** (BASF). The UV-A and UV-B filters may of course also be used in the form of mixtures. Besides the soluble substances mentioned, insoluble pigments, i.e. finely dispersed metal oxides or salts, may also be used for this purpose. Examples of suitable metal oxides are, in particular, zinc oxide and titanium dioxide and also oxides of iron, zirconium, silicon, manganese, aluminium and cerium and mixtures thereof. Silicates (talcum), barium sulfate and zinc stearate may be used as salts. The oxides and salts are used in the form of the pigments for skin-care and skin-protecting emulsions. The particles should have an average diameter of less than 100 nm, preferably from 5 to 50 nm and more preferably from 15 to 30 nm. They may be spherical in shape although ellipsoidal particles or other non-spherical particles may also be used. The pigments may also be surface-treated, i.e. hydrophilicized or hydrophobicized. Typical examples are coated titanium dioxides such as, for example, Titandioxid T 805 (Degussa) or Eusolex® T2000 (Merck). Suitable hydrophobic coating materials are, above all, silicones and particularly trialkoxyoctyl silanes or simethicones. So-called micro- or nanopigments are preferably used in sun protection products. Micronized zinc oxide is preferably used. Other suitable UV filters can be found in P. Finkel's review in **SÖFW-Journal 122, 543 (1996)**.

Besides the two above-mentioned groups of primary protection factors, secondary protection factors of the **antioxidant** type may also be used. Secondary sun protection factors of the antioxidant type interrupt the photochemical reaction chain which is initiated when UV rays penetrate into the skin. Typical examples of suitable antioxidants are amino acids (for

example glycine, histidine, tyrosine, tryptophane) and derivatives thereof, imidazoles (for example urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (for example anserine), carotinoids, carotenes (for example α-carotene, β-carotene, lycopene) and derivatives thereof, chlorogenic acid and derivatives thereof, liponic acid and derivatives thereof (for example dihydroliponic acid), aurothioglucose, propylthiouracil and other thiols (for example thioredoxine, glutathione, cysteine, cystine, cystamine and glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl, γ-linoleyl, cholesteryl and glyceryl esters thereof) and their salts, dilaurylthiodipropionate, distearylthiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulfoximine compounds (for example butionine sulfoximines, homocysteine sulfoximine, butionine sulfones, penta-, hexa- and hepta-thionine sulfoximine) in very small compatible dosages (for example pmole to μmole/kg), also (metal) chelators (for example α-hydroxyfatty acids, palmitic acid, phytic acid, lactoferrine), α-hydroxy acids (for example citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (for example γ-linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives thereof (for example ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (for example vitamin E acetate), vitamin A and derivatives (vitamin A palmitate) and coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, α-glycosyl rutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiac resin acid, nordihydroguaiaretic acid, trihydroxy-butyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, Superoxid-Dismutase, zinc and derivatives thereof (for example

ZnO, $ZnSO_4$), selenium and derivatives thereof (for example selenium methionine), stilbenes and derivatives thereof (for example stilbene oxide, trans-stilbene oxide) and derivatives of these active substances suitable for the purposes of the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids).

In addition, **hydrotropes**, for example ethanol, isopropyl alcohol or polyols, may be used to improve flow behavior. Suitable polyols preferably contain 2 to 15 carbon atoms and at least two hydroxyl groups. The polyols may contain other functional groups, more especially amino groups, or may be modified with nitrogen. Typical examples are

- glycerol;
- alkylene glycols such as, for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and polyethylene glycols with an average molecular weight of 100 to 1000 dalton;
- technical oligoglycerol mixtures with a degree of self-condensation of 1.5 to 10 such as, for example, technical diglycerol mixtures with a diglycerol content of 40 to 50% by weight;
- methylol compounds such as, in particular, trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol;
- lower alkyl glucosides, particularly those containing 1 to 8 carbon atoms in the alkyl group, for example methyl and butyl glucoside;
- sugar alcohols containing 5 to 12 carbon atoms, for example sorbitol or mannitol,
- sugars containing 5 to 12 carbon atoms, for example glucose or sucrose;
- amino sugars, for example glucamine;
- dialcoholamines, such as diethanolamine or 2-aminopropane-1,3-diol.

Suitable **preservatives** are, for example, phenoxyethanol, formaldehyde solution, parabens, pentanediol or sorbic acid and the other classes of compounds listed in Appendix 6, Parts A and B of the Kosmetikverordnung ("Cosmetics Directive"). Suitable **insect repellents** are N,N-diethyl-m-toluamide, pentane-1,2-diol or Ethyl Butylacetyl-aminopropionate. A suitable **self-tanning agent** is dihydroxyacetone.

Suitable **perfume oils** are mixtures of natural and synthetic fragrances. Natural fragrances include the extracts of blossoms (lily, lavender, rose, jasmine, neroli, ylang-ylang), stems and leaves (geranium, patchouli, petitgrain), fruits (anise, coriander, caraway, juniper), fruit peel (bergamot, lemon, orange), roots (nutmeg, angelica, celery, cardamon, costus, iris, calmus), woods (pinewood, sandalwood, guaiac wood, cedarwood, rosewood), herbs and grasses (tarragon, lemon grass, sage, thyme), needles and branches (spruce, fir, pine, dwarf pine), resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials, for example civet and beaver, may also be used. Typical synthetic perfume compounds are products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Examples of perfume compounds of the ester type are benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl cyclohexylacetate, linalyl acetate, dimethyl benzyl carbinyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethylmethyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. Ethers include, for example, benzyl ethyl ether while aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal. Examples of suitable ketones are the ionones, α-isomethylionone and methyl cedryl ketone. Suitable alcohols are anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenylethyl alcohol and terpineol. The hydrocarbons mainly include the terpenes and balsams. However, it is preferred to use mixtures of different

perfume compounds which, together, produce an agreeable fragrance. Other suitable perfume oils are essential oils of relatively low volatility which are mostly used as aroma components. Examples are sage oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime-blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavendin oil. The following are preferably used either individually or in the form of mixtures: bergamot oil, dihydromyrcenol, lilial, lyral, citronellol, phenylethyl alcohol, α-hexylcinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, Boisambrene Forte, Ambroxan, indole, hedione, sandelice, citrus oil, mandarin oil, orange oil, allylamyl glycolate, cyclovertal, lavendin oil, clary oil, β-damascone, geranium oil bourbon, cyclohexyl salicylate, Vertofix Coeur, Iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat.

Suitable **dyes** are any of the substances suitable and approved for cosmetic purposes as listed, for example, in the publication "**Kosmetische Färbemittel**" of the **Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106.** These dyes are normally used in concentrations of 0.001 to 0.1% by weight, based on the mixture as a whole.

The total percentage content of auxiliaries and additives may be from 1 to 50% by weight and is preferably from 5 to 40% by weight, based on the particular formulation. The formulations may be produced by standard hot or cold processes and are preferably produced by the phase inversion temperature method.

Examples

To produce the nanoscale metal soaps (**Examples 1 to 5**), carbon dioxide was first taken from a reservoir under a constant pressure of 60 bar and was purified in a column with an active carbon and a molecular sieve

packing. After liquefaction, the CO_2 was compressed to the required supercritical pressure p by a diaphragm pump at a constant delivery rate of 3.5 l/h. The solvent was then brought to the necessary temperature T1 in a preheater and was introduced into an extraction column (steel, 400 ml) charged with the chitosan or chitosan derivative. The resulting supercritical, i.e. fluid, mixture was sprayed through a laser-drawn nozzle (length 830 µm, diameter 45 µm) at a temperature T2 into a Plexiglas expansion chamber containing a 4% by weight aqueous solution of an emulsifiers or protective colloid. The fluid medium evaporated, leaving the dispersed nanoparticles encapsulated in the protective colloid behind. To produce the nanoparticles in accordance with **Example 6**, a 1% by weight dispersion of calcium stearate was added dropwise with vigorous stirring under a reduced pressure of 40 mbar to a 4% by weight aqueous solution of Coco Glucosides. The evaporating solvent was condensed in a cold trap while the dispersion containing the nanoparticles remained behind. The process conditions and the average particle size range (as determined photometrically by the 3-WEM method) are set out in Table 1 below.

Table 1 - Nanoparticles

Ex.	Metal soap	Solvent	p bar	T1 °C	T2 °C	Emulsifier/ protective colloid	PSR nm
1	Magnesium stearate	CO_2	200	80	175	Polyvinyl alcohol	60-120
2	Aluminium stearate	CO_2	180	70	160	Polyethylene glycol (M = 400)	75-120
3	Zinc stearate	CO_2	200	85	180	Polyvinyl alcohol	75-130
4	Zinc hydroxystearate	CO_2	200	85	175	Polyvinyl alcohol	60-140
5	Calcium ricinoleate	CO_2	200	85	175	Coco Glucosides	55-140
6	Calcium stearate	-	-	-	-	Coco Glucosides	60-130

Table 2 below contains a number of Formulation Examples using metal soap nanoparticles.

Table 2

Cosmetic preparations (water, preservative to 100% by weight)

Composition (INCI)	1	2	3	4	5	6	7	8	9	10
Texapon® NSO Sodium Laureth Sulfate	-	-	-	-	-	-	38.0	38.0	25.0	-
Texapon® SB 3 Disodium Laureth Sulfosuccinate	-	-	-	-	-	-	-	-	10.0	-
Plantacare® 818 Coco Glucosides	-	-	-	-	-	-	7.0	7.0	5.0	-
Plantacare® PS 10 Sodium Laureth Sulfate (and) Coco Glucosides	-	-	-	-	-	-	-	-	-	16.0
Dehyton® PK 45 Cocamidopropyl Betaine	-	-	-	-	-	-	-	-	10.0	-
Dehyquart® A Cetrimonium Chloride	2.0	2.0	2.0	2.0	4.0	4.0	-	-	-	-
Dehyquart L® 80 Dococylmethylethoxymonium Methosulfate (and) Propyleneglycol	1.2	1.2	1.2	1.2	1.5	1.5				
Eumulgin® B2 Ceteareth-20	0.8	0.8	-	0.8	-	1.0	-	-	-	-
Eumulgin® VL 75 Lauryl Glucoside (and) Polyglyceryl-2 Polyhydroxystearate (and) Glycerin	-	-	0.8	-	0.8	-	-	-	-	-
Lanette® O Cetearyl Alcohol	2.5	2.5	2.5	2.5	3.0	2.5	-			
Cutina® GMS Glyceryl Stearate	0.5	0.5	0.5	0.5	0.5	1.0	-	-	-	
Cetiol® HE PEG-7 Glyceryl Cocoate	1.0	-	-	-	-	-	-	-	1.0	
Cetiol® PGL Hexyldecanol (and) Hexyldecyl laurate		1.0	-	-	1.0	-	-	-	-	-
Cetiol® V Decyl Oleate	-	-	-	1.0	-	-	-	-	-	-
Eutanol® G Octyldodecanol	-	-	1.0	-	-	1.0	-	-	-	-
Nutrilan® Keratin W Hydrolyzed Keratin	-	-	-	2.0	-	-	-	-	-	-
Lamesoft® LMG Glyceryl Laurate (and) Potassium Cocoyl Hydrolyzed Collagen	-	-	-	-	-	-	3.0	2.0	4.0	-
Euperlan® PK 3000 AM Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	-	-	-	-	-	-	-	3.0	5.0	5.0
Generol® 122 N Soya Sterol					1.0	1.0	-	-	-	-
Nano-aluminium stearate of Example2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Hydagen® CMF Chitosan	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Copherol® 12250 Tocopherol Acetate	-	-	0.1	0.1	-	-	-	-	-	-
Arlypon® F Laureth-2	-						3.0	3	1	
Sodium Chloride	-	-	-	-	-	-	-	1.5	-	1.5

(1-4) hair rinse, (5-6) conditioner, (7-8) shower bath, (9) shower gel, (10) wash lotion

Table 2 (continued)

Cosmetic preparations (water, preservative to 100% by weight)

Composition (INCI)	11	12	13	14	15	16	17	18	19	20
Texapon® NSO Sodium Laureth Sulfate	20.0	20.0	12.4	-	25.0	11.0	-	-	-	-
Texapon® K 14 S Sodium Myreth Sulfate	-	-	-	-	-	-	-	-	11.0	25.0
Texapon® SB 3 Disodium Laureth Sulfosuccinate	-	-	-	-	-	7.0	-	-	-	-
Plantacare® 818 Coco Glucosides	5.0	5.0	4.0	-	-	-	-	-	8.0	4.0
Plantacare® 2000 Decyl Glucoside	-	-	-	-	5.0	4.0	-	-	-	-
Plantacare® PS 10 Sodium Laureth Sulfate (and) Coco Glucosides	-	-	-	40.0	-	-	16.0	17.0	-	-
Dehyton® PK 45 Cocamidopropyl Betaine	20.0	20.0	-	-	8.0	-	-	-	-	7.0
Eumulgin® B1 Ceteareth-12	-	-	-	-	1.0	-	-	-	-	-
Eumulgin® B2 Ceteareth-20	-	-	-	1.0	-	-	-	-	-	-
Lameform® TGI Polyglyceryl-3 Isostearate	-	-	-	4.0	-	-	-	-	-	-
Dehymuls® PGPH Polyglyceryl-2 Dipolyhydroxystearate	-	-	1.0	-	-	-	-	-	-	-
Monomuls® 90-L 12 Glyceryl Laurate	-	-	-	-	-	-	-	-	1.0	1.0
Cetiol® HE PEG-7 Glyceryl Cocoate	-	0.2	-	-	-	-	-	-	-	-
Eutanol® G Octyldodecanol	-	-	-	3.0	-	-	-	-	-	-
Nutrilan® Keratin W Hydrolyzed Keratin	-	-	-	-	-	-	-	-	2.0	2.0
Nutrilan® I Hydrolyzed Collagen	1.0	-	-	-	-	2.0	-	2.0	-	-
Lamesoft® LMG Glyceryl Laurate (and) Potassium Cocoyl Hydrolyzed Collagen	-	-	-	-	-	-	-	-	1.0	-
Lamesoft® 156 Hydrogenated Tallow Glyceride (and) Potassium Cocoyl Hydrolyzed Collagen	-	-	-	-	-	-	-	-	-	5.0
Gluadin® WK Sodium Cocoyl Hydrolyzed Wheat Protein	1.0	1.5	4.0	1.0	3.0	1.0	2.0	2.0	2.0	-
Euperlan® PK 3000 AM Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	5.0	3.0	4.0	-	-	-	-	3.0	3.0	-
Panthenol	-	-	1.0	-	-	-	-	-	-	-
Arlypon® F Laureth-2	2.6	1.6	-	1.0	1.5	-	-	-	-	-
Nano-aluminium stearate of Example 2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Hydagen® CMF Chitosan	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sodium Chloride	-	-	-	-	-	1.6	2.0	2.2	-	3.0
Glycerin (86% by weight)	-	5.0	-	-	-	-	-	1.0	3.0	-

(11-14) "two-in-one" shower bath, (15-20) shampoo

Table 2 (continued)

Cosmetic preparations (water, preservative to 100% by weight)

Composition (INCI)	21	22	23	24	25	26	27	28	29	30
Texapon® NSO										
Plantacare® 818										
Coco Glucosides										
Plantacare® PS 10										
Sodium Laureth Sulfate (and) Coco Glucosides										
Dehyton® PK 45										
Cocamidopropyl Betaine										
Emulgade® SE										
Glyceryl Stearate (and) Ceteareth 12 20 (and) Cetearyl Alcohol (and) Cetyl Palmitate										
Eumulgin® B1										
Ceteareth 12										
Lameform® TGI										
Polyglyceryl-3 Isostearate										
Dehymuls® PGPH										
Polyglyceryl-2 Dipolyhydroxystearate										
Monomuls® 90-O 18										
Glyceryl Oleate										
Cetiol® HE	2.0			2.0	5.0					2.0
PEG-7 Glyceryl Cocoate										
Cetiol® OE									5.0	5.0
Dicaprylyl Ether										
Cetiol® PGL								3.0	10.0	9.0
Hexyldecanol (and) Hexyldecyl Laurate										
Cetiol® SN						3.0	3.0			
Cetearyl Isononanoate										
Cetiol® V						3.0	3.0			
Decyl Oleate										
Myritol® 318								3.0	5.0	5.0
Coco Caprylate Caprate										
Bees Wax									5.0	5.0
Nutrilan® Elastin E20						2.0				
Hydrolyzed Elastin										
Nutrilan® I-50					2.0		2.0			
Hydrolyzed Collagen										
Gluadin® AGP	0.5	0.5	0.5					0.5		
Hydrolyzed Wheat Gluten										
Gluadin® WK	2.0	2.0	2.0	2.0	5.0				0.5	0.5
Sodium Cocoyl Hydrolyzed Wheat Protein										
Euperlan® PK 3000 AM	5.0			5.0						
Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine										
Arlypon® F										
Laureth-2										
Nano-aluminium stearate of Example 2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Hydagen® CMF	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Chitosan										
Magnesium Sulfate Hepta Hydrate									1.0	1.0
Glycerin (85% by weight)						3.0	3.0	5.0	5.0	3.0

(21-25) foam bath, (26) soft cream, (27,28) moisturizing emulsion, (29,20) night cream

Table 2 (continued)

Cosmetic preparations (water, preservative to 100% by weight)

Composition (INCI)	31	32	33	34	35	36	37	38	39	40
Dehymuls® PGPH Polyglyceryl-2 Dipolyhydroxystearate	4									
Lameform® TGI Polyglyceryl-3 Diisostearate	2.0									
Emulgade® PL 68/50 Cetearyl Glucoside (and) Cetearyl Alcohol	-	-	-	-	4.0	-	-	-	3.0	-
Eumulgin® B2 Ceteareth-20	-	-	-	-	-	-	-	-	-	-
Tegocare® PS Polyglyceryl-3 Methylglucose Distearate	-	-	3.0	-	-	-	4.0	-	-	-
Eumulgin VL 75 Polyglyceryl-3 Diisostearate/IPS/Lauryl Glucoside (and) Glycerin	-	-	-	-	-	3.0	-	-	2.0	-
Bees Wax	-	-	-	-	-	-	-	-	-	-
Cutina® GMS Glyceryl Stearate	-	-	-	-	-	2.0	4.0	-	-	4.0
Lanette® O Cetearyl Alcohol	-	-	2.0	-	2.0	4.0	2.0	4.0	4.0	1.0
Antaron® V 216 PVP/Hexadecene Copolymer	-	-	-	-	-	3.0	-	-	-	2.0
Myritol® 818 Cocoglycerides	5.0	-	10.0	-	8.0	6.0	6.0	-	5.0	5.0
Finsolv® TN C12/15 Alkyl Benzoate	-	5.0	-	2.0	-	-	3.0	-	-	2.0
Cetiol® J 600 Oleyl Erucate	7.0	4.0	3.0	5.0	4.0	3.0	3.0	-	5.0	4.0
Cetiol® OE Dicaprylyl Ether	9.0	-	5.0	8.0	8.0	5.0	4.0	3.0	4.0	6.0
Mineral Oil	-	4.0	-	4.0	-	2.0	-	1.0	-	-
Cetiol® PGL Hexadecanol (and) Hexyldecyl Laurate	-	7.0	3.0	7.0	4.0	-	-	-	1.0	-
Panthenol/bisabolol	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Nano-aluminium stearate of Example 2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Hydagen® CMF Chitosan	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Copherol® F 1300 Tocopherol / Tocopheyl Acetate	0.5	1.0	1.0	2.0	1.0	1.0	1.0	2.0	0.5	2.0
Neo Heliopan® Hydro Sodium Phenylbenzimidazole Sulfonate	3.0	-	-	3.0	-	-	2.0	-	2.0	-
Neo Heliopan® 303 Octocrylene	-	5.0	-	-	-	4.0	5.0	-	-	10.0
Neo Heliopan® BB Benzophenone-3	1.5	-	-	2.0	1.5	-	-	-	2.0	-
Neo Heliopan® E 1000 Isoamyl p-Methoxycinnamate	5.0	-	4.0	-	2.0	2.0	4.0	10.0	-	-
Neo Heliopan® AV Octyl Methoxycinnamate	4.0	-	4.0	3.0	2.0	3.0	4.0	-	10.0	2.0
Uvinol® T 150 Octyl Triazone	2.0	4.0	3.0	1.0	1.0	1.0	4.0	3.0	3.0	3.0
Zinc Oxide	-	6.0	6.0	-	4.0	-	-	-	-	5.0
Titanium Dioxide	-	-	-	-	-	-	-	5.0	-	-
Glycerin (86% by weight)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

(31) w/o sun protection cream, (32-34) w/o sun protection lotion, (35,38,40) o/w sun protection lotion, (36,37,39) o/w sun protection cream